

GAS-PHASE COMBUSTION SYNTHESIS OF ALUMINUM NITRIDE POWDER

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Due to its combined properties of high electrical resistivity and high thermal conductivity, aluminum nitride (AlN) is a highly desirable material for electronics applications. Methods are being sought for synthesis of unagglomerated, nanometer-sized powders of this material, prepared in such a way that they can be consolidated into solid compacts having minimal oxygen content. A procedure for synthesizing these powders through gas-phase combustion is described. This novel approach involves reacting AlCl_3 , NH_3 , and Na vapors. Equilibrium thermodynamic calculations show that 100% yields can be obtained for these reactants with the products being AlN, NaCl, and H_2 . The NaCl by-product is used to coat the AlN particles in situ. The coating allows for control of AlN agglomeration and protects the powders from hydrolysis during post-flame handling. On the basis of thermodynamic and kinetic considerations, two different approaches were employed to produce the powder, in co-flow diffusion flame configurations. In the first approach, the three reactants were supplied in separate streams. In the second, the AlCl_3 and NH_3 were premixed with HCl and then reacted with Na vapor. X-ray diffraction (XRD) spectra of as-produced powders show only NaCl for the first case and NaCl and AlN for the second. After annealing at 775 °C under dynamic vacuum, the salt was removed and XRD spectra of powders from both approaches show only AlN. Aluminum metal was also produced in the co-flow flame by reacting AlCl_3 with Na. XRD spectra of as-produced powders show the products to be only NaCl and elemental aluminum.

Introduction

Background on AlN

Due to its unique physical properties, aluminum nitride (AlN) has been considered for many applications, from piezoelectric materials to matrix materials for a composite uranium nitride nuclear fuel. The largest market for AlN is in the electronics industry. This interest stems from the need to develop electronics substrates with high thermal and low electrical conductivities. Few materials possess such properties. Of those that do, AlN is the most desirable for reasons of safety and cost [1]. As a ceramic, AlN has a high electrical resistivity ($r > 10^{13} \Omega \cdot \text{cm}$) while possessing a theoretical thermal conductivity comparable to copper ($k = 319 \text{ W/m} \cdot \text{K}$). The potential market for AlN in electronics applications alone is predicted to be \$550 million by the year 2000 [2].

The current commercial methods for producing AlN—carbothermal reduction and direct nitridation [3]—yield fine powders that can be further processed by, for example, sintering or hot-pressing to produce solid compacts. Carbothermal reduction is a batch process involving a high-temperature (1400–1800 °C), solid–solid reaction between alumina and carbon powders in a nitrogen atmosphere, yielding AlN powders with particle diameters of 0.01–3.0 μm [1,3]. AlN production via direct nitridation is also a

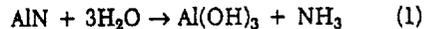
batch process and involves reacting aluminum powder with nitrogen gas at temperatures in excess of 1200 °C, to produce powders with particle diameters in the range of 0.3–12 μm [3,4].

Challenges in AlN Production

There is a great need for new synthesis routes for the production of AlN due to the inherent limitations of present production processes. Both carbothermal reduction and direct nitridation employ precursors that contain oxygen: aluminum oxide and aluminum powders, respectively (aluminum powders inherently contain oxygen in the surface layer and lattice). Furthermore, both processes include steps that expose the AlN product powders to oxygen and other contaminants: excess carbon is burned off during carbothermal reduction, whereas direct nitridation employs at least one grinding step, which introduces oxygen and metallic impurities [3]. Oxygen impurities dramatically decrease the thermal conductivity of AlN. For example, the thermal conductivity of AlN with 300 ppm oxygen is 280 $\text{W/m} \cdot \text{K}$, whereas with 0.8 wt % oxygen, it reduces to 80 $\text{W/m} \cdot \text{K}$ [5].

Another challenge in the production of AlN is the reduction of particle size in order to exploit superplastic-forming (SPF). Since SPF rates increase with decreasing grain size, it is desirable to identify commercially viable methods of synthesizing nanometer-

sized (2–100 nm) powders of AlN. However, the high surface-to-volume ratio for these powders has heretofore resulted in excessive oxygen contamination due to surface hydrolysis via



which occurs when AlN is exposed to moisture. To produce AlN powder that is useful in high thermal conductivity applications, the process must yield powders that are free of impurities and not susceptible to surface hydrolysis during subsequent handling.

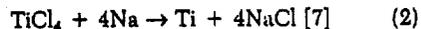
Another important criterion for AlN applications is that the starting powders be unagglomerated or weakly agglomerated to ensure that the resulting compacts can be sintered to near-theoretical density. Flames generally produce powders composed of long-chain, hard agglomerates. These powders are not easily compacted, resulting in materials with high void fractions and greatly diminished properties. Recently, Axelbaum et al. have developed a flame process, applicable to a broad class of materials, for synthesizing *unagglomerated, unoxidized* nanometer-sized particles [6]. In this paper, the process is extended to the synthesis of AlN.

Particle-Coating to Prevent Agglomeration and Oxygen Contamination

The approach to prevent agglomeration in flames is to allow nucleation and growth of *primary particles* to proceed normally, until they have grown to a desired size, and then encapsulate these particles with an appropriate material before they excessively agglomerate. Upon subsequent collisions, the coated particles will agglomerate, but the primary particles within them will not. When the coating is later removed, the resulting powder will contain unagglomerated or weakly agglomerated particles of the specified size.

In addition to controlling size, the particle coating also protects oxygen- and moisture-sensitive primary particles during post-flame handling. Thus, ultrafine, nonoxide particles produced in an oxygen-free environment can be handled without extreme precautions.

This flame and coating procedure has been demonstrated in a sodium halide flame for the synthesis of titanium metal powders [6]. The reaction employed is given by



Sodium halide reactions such as this can be applied to produce a variety of materials, including metals, intermetallics, ceramics, and composites. Calcote and Felder have produced high-purity solid silicon [7], and Glassman et al. have produced TiN, TiB₂, TiC, TiSi₂, SiC, and B₄C [8]. Axelbaum et al. have extended these works and produced Ti, TiB₂, W, and

W-Ti [6,9,10], with emphasis on producing unagglomerated, nanometer-sized powders by employing the coating procedure described above. The coating material for particles produced in sodium halide flames is conveniently the sodium chloride by-product. Sodium chloride is an effective coating because its boiling point is 1410 °C, which allows condensation to be triggered in the flame by controlling temperature and NaCl concentration. Furthermore, it is possible to exploit the Kelvin effect to control the onset of coating and attain control of particle size for particles <40 nm in diameter [6]. Finally, the NaCl coating can be easily removed by washing with an appropriate solvent or through vacuum sublimation at moderate temperatures (~800 °C).

The sodium halide flame and coating process should be well suited for production of AlN powders with low oxygen content. The reaction precursors are oxygen free, and the salt by-product is produced in the reaction zone simultaneously with the primary-product particles, with coating occurring on a millisecond time scale. The coating should then allow the particles to be conveniently handled without acquiring the oxygen impurities that can be so deleterious to the thermal conductivity of AlN.

Thermodynamics

One approach to producing AlN that has received considerable attention recently is the gas-phase reaction of AlCl₃ with NH₃. Kimura et al. [11], Park et al. [12], and Riedel and Gaudl [13] produced AlN powders with this reaction, and Lewis [14], Nickel et al. [15], and Riedel and Gaudl [13] produced films by chemical vapor deposition (CVD). There are a number of difficulties associated with this endothermic (35.5 kJ/mole) reaction, as can be seen from the equilibrium composition for



shown in Fig. 1. These results were obtained using commercial software and verified with the NASA equilibrium code. The yields for this chemistry are only modest, typically <30% with stoichiometric NH₃. Yields increase with increasing NH₃ or N₂; however, over 50 times stoichiometric NH₃ is needed to approach 100% yields [16]. Nickel et al. have shown that the primary reason for the low yield of Eq. (3) is the decomposition of NH₃ [15]. With no decomposition, near-perfect yields are achieved thermodynamically. Physically, it is possible to reduce the extent of ammonia decomposition by proper selection of reactor materials and formation of stable AlCl₃·(NH₃)_n (n = 1–6) adducts [12]. By employing these measures, yields of up to 70% have been achieved with 6 times stoichiometric NH₃ at moderate temperatures (1000 °C) [14]. An inherent limitation of this chemistry is that the reactor tem-

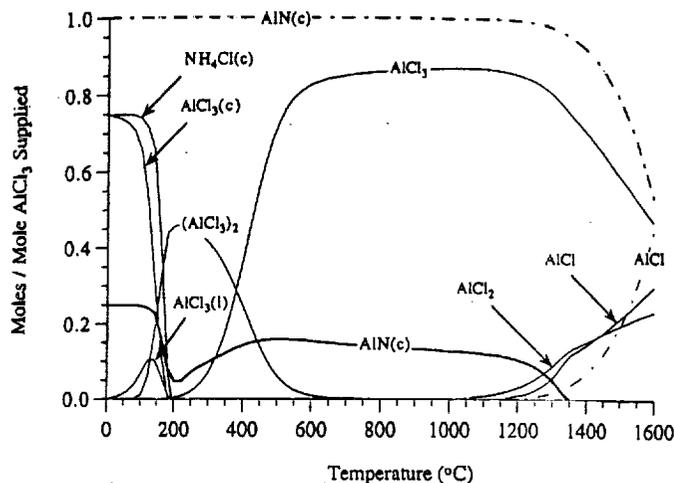
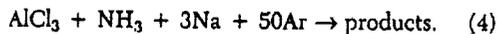


FIG. 1. Equilibrium compositions as functions of temperature for mixtures of $\text{AlCl}_3 + \text{NH}_3 + 50\text{Ar}$ (solid lines) and $\text{AlCl}_3 + \text{NH}_3 + 3\text{Na} + 50\text{Ar}$ (dashed lines).

perature must be high to obtain reasonable production rates; however, high temperature promotes NH_3 decomposition, which limits yield [12]. Also, Riedel et al. have shown that the resulting fine powders contain ~3 wt % oxygen due to hydrolysis [13].

The addition of Na to the $\text{AlCl}_3\text{-NH}_3$ system can greatly enhance thermodynamic yield, with or without NH_3 decomposition. Adding stoichiometric Na to the reaction in Eq. (3) results in



The equilibrium products for this reaction are shown in Fig. 1. The adiabatic flame temperature for Eq. (4) is 1225 °C when the reactant temperature is 650 °C. Nonetheless, radiative heat transfer can be so significant in these flames that the product temperature can be controlled by the temperature of the combustion chamber. Thus, product composition is reported as a function of temperature in Fig. 1. The results reveal that 100% yields are achieved with this system over a wide range of temperatures. In addition to high yield, Eq. (4) has many other practical advantages over Eq. (3). First, the by-product NaCl can be incorporated as a coating material, as discussed above, to avoid agglomeration and oxygen contamination during post-synthesis handling. Second, it is overall exothermic (-1244 kJ/mole), resulting in lower energy costs. And third, the gaseous by-product is hydrogen, which can be used for its high heating value, as compared to HCl, which must be scrubbed.

Experimental Considerations

For the three reacting species shown in Eq. (4), two possible schemes exist for mixing: either the reactants can be supplied in three separate co-flowing streams or two of the reactants can be premixed and

then this mixture can be reacted with the third. The second scheme presumes that the two premixed reactants will not react to form an unacceptable product, for example, a solid phase that will either plate out on the walls or lead to inhomogeneities in the final product. AlCl_3 and NH_3 will react below 225 °C to form AlN(s) and $\text{NH}_4\text{Cl(s)}$, as shown in Fig. 1. Above 225 °C, the only condensed phase is AlN(s) . Thus, mixing AlCl_3 and NH_3 would not appear promising because condensed phases would form in the supply lines. Similarly, AlCl_3 reacts hypergolically with Na to form Al and NaCl, thereby making this mixture infeasible. The possibility of mixing NH_3 and Na has been considered, but preliminary studies revealed that NH_3 decomposition is excessive and that a solid phase, possibly NaH, is formed.

Thus, it would appear that the three reactants have to be supplied to the burner in separate jets, and this approach, referred to as case A, is considered. However, an alternative approach, wherein the reaction of AlCl_3 and NH_3 is suppressed, is also examined. When AlCl_3 and NH_3 are mixed at 400 °C, stable $\text{AlCl}_3 \cdot (\text{NH}_3)_n$ adducts are formed [17], and these adducts decompose into AlN and HCl above 700 °C [14]. Incomplete conversion to the adduct results in AlN(s) and HCl(g) production as shown in Fig. 1, which is not acceptable. Nonetheless, by adding HCl to the reactants, the forward reaction, which produces AlN , can be suppressed. Following this reasoning, it is possible to supply a purely gaseous mixture of AlCl_3 , NH_3 , and HCl that will then react with Na. This approach is considered and will be referred to as case B.

The basic characteristics of the co-flow sodium flame used in this study have been described previously for the production of titanium and titanium diboride [6]. Only modifications and improvements will be described. Configuration 1, shown in Fig. 2,

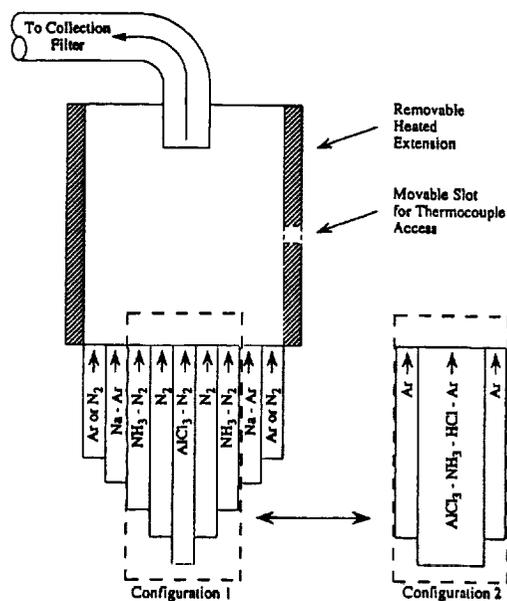


FIG. 2. Schematic diagram illustrating two different burner configurations employed to produce AlN and Al.

is for case A, where all three reactants are supplied separately. It consists of five heated, concentric tubes, all stainless steel, except for the innermost tube, which is quartz. The tubes have outside/inside diameters of 3.1/1.9, 6.4/4.6, 12.7/10.9, 25.4/19.1, and 75/70 mm, respectively. All reactants are introduced in the vapor phase. The halide is introduced through the central tube, followed by inert, then NH_3 , and then Na. An inert shroud gas is supplied in the outermost annular section. The reaction zone occurs in the mixing layer of the reactants, with the inner inert stream acting as a diffusion barrier near the base to avoid particle deposition at the burner mouth. The outer shroud ensures a uniform flow and isolates the flame from room air. Honeycomb is placed at the exits to ensure uniform laminar flows.

The configuration for case B, where AlCl_3 , NH_3 , and HCl are premixed, is as shown in the inset of Fig. 2. In this configuration, the 3.1/1.9-mm quartz tube is removed, and the 6.4/4.6-mm stainless steel tube is replaced with a graphite tube with outside/inside diameters of 7.5/5.0 mm, respectively.

Sodium is metered in the liquid phase with a stainless steel syringe pump. Supplying sodium with a positive displacement pump is necessary to ensure that a line failure would not lead to an uncontrolled release of liquid sodium. The liquid sodium is fed to the interior of a sintered, stainless steel tube where it wicks through and wets the outer walls. Argon, supplied to the exterior of the porous tube, carries the sodium vapor to the burner.

Aluminum chloride powder is stored in a temper-

ature-controlled monel reservoir. Nitrogen or argon carrier gas is metered by a mass flow controller and then bubbled through the aluminum chloride powder, after which it is assumed to be saturated with aluminum chloride vapor.

A heated, insulated, stainless steel extension is attached to the outermost tube of the burner. The extension acts to minimize heat loss from the burner surface and the flame and to prevent entrainment of oxygen. The extension contains a slot in the axial direction to allow for thermocouple measurements.

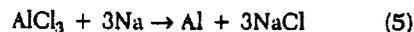
The plumes emanating from these flames are well-defined streams of particles akin to soot emanating from an inverse-co-flow hydrocarbon flame [18]. The particles are collected into a 1.2-cm-diameter stainless steel tube located approximately 6 cm above the burner rim. The particles are extracted under near-isokinetic conditions and collected on a 10- μm porous stainless steel filter. After collection, the particles are scraped from the filter and placed in storage vials under an inert atmosphere.

Flame temperatures are obtained with Pt-6%Rh/Pt-30%Rh thermocouples (type B). The wire size is 0.05 mm, and the thermocouple wires and bead are bare. The rapid insertion technique is employed to minimize particle buildup on the thermocouple and to limit exposure to the hostile environment. Due to the relatively low temperatures in these flames, radiation corrections were not made.

Particle composition is analyzed with a Rigaku horizontal X-ray diffractometer (XRD). The Scherrer formula, which is based on the inverse relationship between XRD peak width and particle size, is used to determine nominal particle size.

Experimental Results

Prior to synthesizing AlN, elemental aluminum was produced via



The burner was configured as shown in Fig. 2 for configuration 2. The AlCl_3 vapor with Ar carrier gas was introduced in the innermost graphite tube, followed by a co-flow of Ar, and then the Na-Ar mixture. The shroud gas in the outermost annulus was Ar.

Operating conditions, shown in Table I, were chosen to ensure the flame was overventilated in Na; i.e., Na vapor was present along the centerline above the luminous flame tip. In accord with thermodynamic calculations, this mode of operation ensures nearly 100% yields because the local stoichiometry will ultimately be sodium-rich along the centerline. The Na- AlCl_3 flame is similar in appearance to that of Na- TiCl_4 [6]. The apparent reaction zone is evident as a thin, yellow luminous zone. The shape of the flame is typical of the Burke-Schumann flame.

TABLE 1
Run conditions and configuration for specified product

Product	Burner Temp (°C)	Species	Total Flow Rate (sccm)	Reactant Concentration
Al	800	AlCl ₃ /Ar	38	0.48/0.52
		Ar (inner co-flow)	1100	—
		Na/Ar	1600	0.10/0.90
AlN (case A)	710	AlCl ₃ /N ₂	160	0.44/0.56
		N ₂ (inner co-flow)	960	—
		NH ₃ /N ₂	2290	0.22/0.78
		Na/Ar	2830	0.10/0.90
AlN (case B)	650	AlCl ₃ /NH ₃ /HCl/Ar	235	0.12/0.15/0.17/0.56
		Ar (inner co-flow)	350	—
		Na/Ar	2750	0.07/0.93

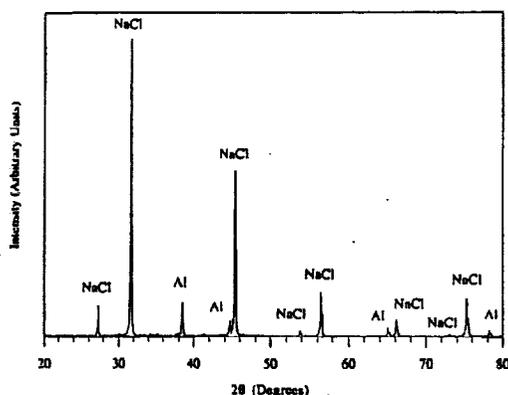


FIG. 3. X-ray diffraction spectra of as-produced powder from an AlCl₃-Na flame under conditions shown in Table 1 and in configuration 1 of Fig. 2.

Buoyancy is negligible in these heavily diluted flames because the flame temperature is only 300–500 °C higher than the reactant and co-flow temperatures.

The as-produced aluminum powder is light gray. A characteristic XRD of the as-produced powders is shown in Fig. 3. XRD peaks index to only Al and NaCl. The nominal diameter of the particles in Fig. 3, as estimated by the Scherrer formula, are 60 nm for Al and 80 nm for NaCl.

Nitrogen was then substituted in place of Ar for the AlCl₃ carrier gas and inner and outer co-flows to determine if AlN might be produced by in situ nitridation of the aluminum particles. Nitridation of Al by N₂ has been reported to begin at temperatures as low as 800 °C but to be very slow at these temperatures. For 15- μ m-diameter aluminum particles at 1550 °C, nitridation occurs within 2 s [2]. For

nanometer-sized particles, the time would be expected to be considerably less. For the run conditions investigated, the flame temperatures did not exceed 1100 °C, and temperatures quickly decreased downstream of the flame due to radiative heat loss and heat loss to the outer shroud gas. Under these conditions, the nitridation reactions appear to be too slow to effectively produce AlN because no AlN peaks were observed in XRD spectra of either the as-produced or the annealed samples.

Employing the chemistry of Eq. (4) and considering the thermodynamic results, AlN was then synthesized using configuration 1 shown in Fig. 2 and experimental conditions of case A. Under these conditions, two reaction zones are expected: an inner reaction zone where NH₃ reacts with AlCl₃ and an outer reaction zone where the products of the inner zone react with Na. Indeed, two thin, distinct particle-formation zones were observed by laser light scattering. Quantitative scattering measurements were not made because of the broad and strong absorption cross section of Na₂ [19].

Powders were collected from the AlCl₃-NH₃-Na flames under various operating conditions. The as-produced powders contain NaCl, with certain run conditions also producing NH₄Cl. As shown in Fig. 1, NH₄Cl is a low-temperature product of the AlCl₃-NH₃ system, and with the addition of stoichiometric Na, NH₄Cl is not present. Thus, if the flame is operated underventilated in Na, NH₄Cl may be produced when the products reach the cooler regions of the sampling system. Unlike the AlCl₃-Na flame, it is difficult to ensure that this flame is overventilated in Na. Samples obtained from runs with Na in excess of the stoichiometric amount show no NH₄Cl peaks in the XRD spectra.

XRD spectra of as-produced powders do not indicate the presence of crystalline AlN. This may be

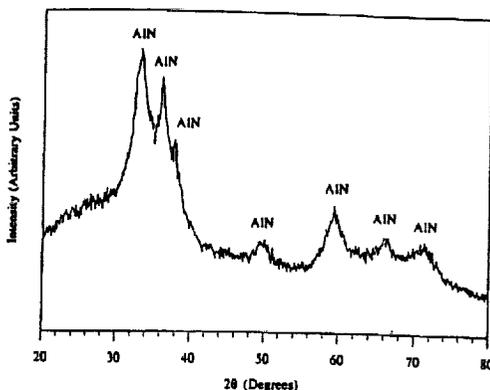


FIG. 4. X-ray diffraction spectra of heat-treated powder produced in an $\text{AlCl}_3\text{-NH}_3\text{-Na-N}_2$ flame under conditions of case A in Table 1 and in configuration 1 of Fig. 2.

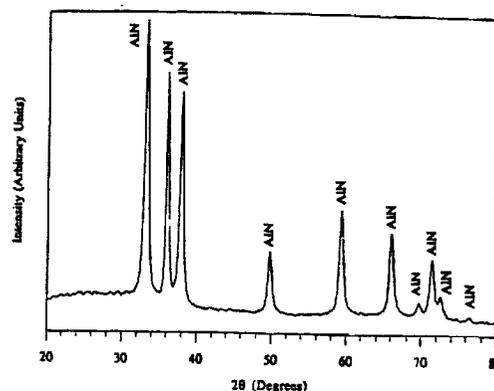


FIG. 6. X-ray diffraction spectra of heat-treated powder produced in an $\text{AlCl}_3\text{-NH}_3\text{-HCl-Na}$ flame under conditions of case B in Table 1 and in configuration 2 of Fig. 2.

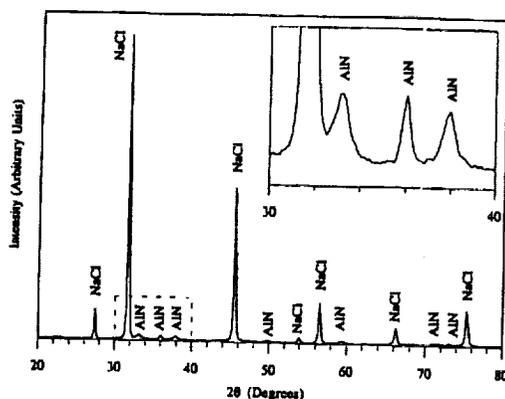


FIG. 5. X-ray diffraction spectra of as-produced powder from an $\text{AlCl}_3\text{-NH}_3\text{-HCl-Na}$ flame under conditions of case B in Table 1 and in configuration 2 of Fig. 2.

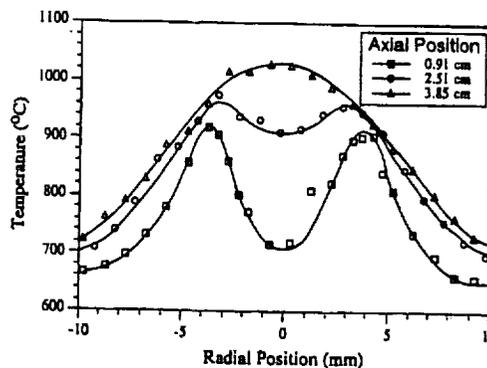


FIG. 7. Radial temperature profiles of an $\text{AlCl}_3\text{-NH}_3\text{-HCl-Na}$ flame at three different axial locations above the burner exit under conditions of case B in Table 1 and in configuration 2 of Fig. 2.

because the AlN is amorphous or the peaks are too small and broad to be detected against the large background of NaCl. As shown in Fig. 4, XRD patterns of powder that were produced under the conditions in Table 1 and heat-treated for 4 h at 775 °C under dynamic vacuum show AlN peaks. The broad peaks indicate that the AlN particles are very small, 6 nm in diameter as estimated by the Scherrer formula.

The two reaction zones associated with separate mixing of the three reactants can potentially lead to a broad range of morphologies because AlN is formed in both zones and under very different conditions—one zone being endothermic and the other exothermic. Uniformity of product is often, though not always, desirable from a materials perspective.

Case B, which results in a single, exothermic re-

action zone, can potentially lead to a more uniform product. Figure 5 shows the XRD spectra of as-produced powders for configuration 2 with operating conditions of case B. The only phases detected are NaCl and AlN. The Scherrer formula predicts a crystal size of 40 nm for the NaCl and 20 nm for the AlN. The taller NaCl peaks are a result of the stoichiometry, which leads to about 4 times as much NaCl as AlN on a molar basis, and the fact that larger-sized particles have taller, narrower peaks. The AlN may also not be fully crystalline. After heat treatment at 775 °C for 4 h under dynamic vacuum, the salt is removed and, as shown in Fig. 6, the only phase present is AlN. No special precautions were necessary to obtain this sample. Prior to heat treatment, the as-produced powders were stored for 4 days in vials filled with Ar. Nonetheless, no oxide, hydroxide, or oxynitride phases are observed.

Radial temperature measurements at three different axial locations are shown in Fig. 7. The basic profiles are consistent with the Burke-Schumann flame, except that the maximum temperatures near the base are significantly lower than at the tip. This result is a consequence of the inert co-flow between the reactant streams. This co-flow is added to avoid particle buildup at the rim by minimizing formation rates of condensed phases in this region. Since the reactants are hypergolic, the burner would rapidly clog if the inner co-flow were not employed.

Due to the significant dilution in this flame, the increase in temperature is only modest, about 400 °C. Accounting for the inner co-flow, the stoichiometric adiabatic flame temperature is 1145 °C, which is consistent with the maximum-measured temperature of 1050 °C.

Conclusions

Nanocrystalline aluminum and aluminum nitride powders have been successfully synthesized for the first time in sodium-halide flames. Aluminum was synthesized by the reaction of AlCl_3 with Na. Aluminum nitride was synthesized by adding Na to the well-known $\text{AlCl}_3\text{-NH}_3$ system. Thermodynamic yields of this system are dramatically improved by the addition of Na, with the by-products of the reaction being NaCl and H_2 . The NaCl has been used to encapsulate the metal and ceramic particles in situ. XRD spectra suggest that the particles are indeed nanoscale, as desired. Despite having handled these high-surface-area powders in air, indications are that the coating has protected them from oxygen contamination, a problem that has plagued AlN production. The Al and AlN powders appear to be single phase, as detected by XRD.

By keeping the AlN particles encased in NaCl until just before consolidation, it is believed that the final compacts will have low oxygen impurities. Thus, this process holds promise as a commercially viable method of producing large quantities of nanocrystalline AlN materials with high thermal conductivities.

Acknowledgments

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